

1,139,115



# PATENT SPECIFICATION

DRAWINGS ATTACHED

1,139,115

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## COMPLETE SPECIFICATION

### Epoxy Resin Sealants

We, W. R. GRACE & Co., a Corporation organised and existing under the laws of the State of Connecticut, United States of America, of 62 Whittemore Avenue, Cambridge 40, Massachusetts, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to epoxide compositions useful as adhesives, particularly for forming metal-to-metal bonds in vacuum-casting apparatus.

In casting ingots of steel and alloys, gas is evolved during solidification of the molten metal to an extent depending upon the composition of the molten metal. In the production of "rimmed" steel, relatively large quantities of gas are present in a substantially uncombined state since deoxidizers are not added to the metal, except for minor amounts of aluminium. During solidification, the uncombined gases are continuously evolved, and this, together with certain other factors, results in a pronounced variation in properties between different sections of the ingot. In the manufacture of "killed" and "semi-killed" steels, oxygen is caused to combine with silicon, aluminium or other deoxidizing agent which is added prior to or during casting of the ingot. Though the steels treated with deoxidizers have a more uniform composition and contain lesser amounts of gas in an uncombined state, enough hydrogen or other gas is present to cause the formation of minute fissures throughout the body of the ingot. Consequently, it is generally desirable to degas the various types of steel in order to obtain ingots of improved quality with respect to both physical and chemical characteristics.

In some metallurgical procedures degassing is carried out before pouring of the ingots by employing a furnace having vacuum means for

removing the gaseous constituents from a bath of molten metal. In other procedures, such as vacuum casting, the gases present in a substantially uncombined state are removed from the molten metal during pouring of the ingots. An especially rapid and efficient method of vacuum casting utilizes an apparatus comprising a pouring box seated on and joined to a mould member with a sealing composition that will provide a temporary airtight seal between the box and mould during pouring of the ingot. In this apparatus a vacuum pump or other evacuating means is connected to a passageway in the lower part of the pouring box so that air can be evacuated from the empty mould and harmful gases can be removed from the stream of molten metal as it is introduced into the mould cavity. After the ingot has been poured, the seal between the box and the mould is broken and the pouring box is detached so that the ingot can be removed.

Satisfactory performance of this type of vacuum casting apparatus depends in large measure on the sealing composition used at the juncture of the pouring box and mould member. In addition to having a workable viscosity to facilitate handling and application, the composition employed must have the adhesive and cohesive properties necessary for forming and maintaining an airtight seal between the metal parts. Also, it is essential that the composition have the ability to cure without bubbling to a tough, elastic mass over a wide temperature range and within a relatively short time. Once the composition has cured, it must be capable of withstanding high temperatures without melting or deteriorating while the ingot is being poured but yet be such that the pouring box may be readily detached after pouring has been completed.

While various types of sealants have been used in vacuum casting procedures, epoxy resin compositions have generally been the most satisfactory where the seal is exposed to high

[Price 4s. 6d.]

temperatures. As is well-known in the art, these compositions are ordinarily prepared and utilized as a two-package system in order to prevent premature curing of the resin during shipment and storage. As supplied, one package contains the resin component and the other package contains the curing component, which components are combined and thoroughly blended at the time of use.

One epoxide sealant which has performed exceptionally well in vacuum casting applications is derived from a first component containing an epoxy novolac resin and a second component containing a resinous polyamide together with an amine curing agent for the epoxy novolac resin. If desired, either or both the resin and curing components may contain an inorganic filler. In comparison to the other epoxy sealants in current use, the above epoxy novolac resin composition possesses, in both its cured and uncured state, superior properties with regard to easy application of the composition and the successful operation of degassing equipment requiring a temporary vacuum-tight seal. However, in view of the various operating procedures and temperatures encountered commercially, it is desirable to increase the flexibility of this composition in its cured state and to accelerate its decomposition time after the ingot has been poured, so that the sealant in the mould groove can be removed with greater ease. Unless the groove is completely free from cured composition, the seal formed from fresh material for the succeeding pouring run tends to crack, which results in a less effective vacuum.

According to the present invention, it has now been found that epoxy novolac resin compositions having improved flexibility and the desired decomposition characteristics are obtained by using a cured epoxy resin derived from (A) 100 parts by weight of a resin mixture of (1) 10 to 50% by weight of an epoxy novolac resin and (2) correspondingly, 50 to 90% by weight of a liquid glycidyl polyether of a polyhydric phenol having an epoxide equivalent weight between 350 and 450, preferably a glycidyl polyether of bis(4-hydroxyphenyl)dimethyl methane having an epoxide equivalent weight between 375 and 410; (B) 30 to 50 parts by weight of finely divided magnesium silicate; (C) between 50 and 100 parts by weight of a liquid resinous polyamide having an amine number of at least 85, and (D) an aliphatic polybasic amine (as hereinafter defined) which is a curing agent for the resin mixture (A) in an amount in excess of that necessary to react stoichiometrically with said resin. It is usually convenient to prepare these cured epoxy resins by mixing together a first resin component comprising constituents (A) and (B) and a second curing component comprising constituents (C) and (D).

The invention is illustrated by the accompanying drawings, in which

Figure 1 is a vertical cross-sectional view of an assembled vacuum casting apparatus with the composition of the present invention forming a seal at the juncture of a removable pouring box and ingot mould; and

Figure 2 is an enlarged fragmentary cross-sectional view of the seal.

Referring now to the Figures, an ingot mould has a cylindrical cavity 2 tapering at its lower end and an annular groove 3 in its upper surface. The groove 3 extends around the circumference of the upper surface of the mould 1 and provides a support for the removable pouring box generally designated at 5. Within the groove 3 is a sealant 4 which is the sealing composition of the present invention. The sealant 4 forms a vacuum-tight seal between the mould 1 and the pouring box 5.

The pouring box 5 is divided by a transverse wall 5c into an upper section comprising a basket 5a for receiving the molten metal to be poured and a lower section comprising a vacuum chamber 5b communicating directly with the mould cavity 2. The transverse wall 5c contains a pouring aperture 6 which is closed by a fusible closure member 7. When molten metal is deposited in the basket 5a, the closure 7 becomes fused and will allow the molten metal to pass through the aperture 6 and through the vacuum chamber 5b into the mould cavity 2. An annular refractory hot top 8 is positioned within the vacuum chamber 5b and is attached to the mould. A tube 9, which is connected to a vacuum pump (not shown), is tightly secured within an opening (not shown) located in the side wall which leads into the vacuum chamber 5b.

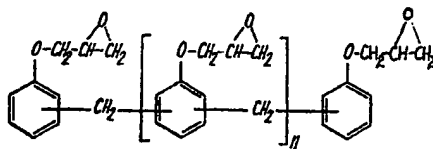
In assembling and operating the apparatus described above, the components of the epoxide sealing composition are deposited in the annular groove contained in the upper surface of the mould body. Thereafter, the pouring box with the aperture in the transverse wall tightly closed by a fusible closure member is seated on the mould so that the lower edge of the vacuum chamber is positioned and embedded in the mass of sealing composition contained within the groove. The assembly is then allowed to stand for a time sufficient to allow complete curing of the composition. The specific time period required depends upon the temperature of the mould being assembled. For the quantity of sealant ordinarily used, curing may be accomplished in about two to seven hours at ambient temperature and in ten minutes or less at a temperature of about 93°C. with somewhat faster curing being obtained with further increases in temperature.

After curing is complete and the aperture tightly closed, the vacuum pump is started, so that air is evacuated and a vacuum created in the mould and vacuum chamber. The molten metal to be poured is deposited in the basket which comprises the upper section of the pouring box using a transporting ladle or other

conventional means. In the presence of the hot metal, the closure member becomes fused and allows the metal to flow through the aperture in the transverse wall and through the vacuum chamber into the mould cavity. Because of the high vacuum exerted in an area close to the stream of metal being introduced, the stream is disrupted into a spray of fine particles from which harmful gases may be readily removed. The effectiveness in removing substantially all the uncombined gases is further aided by the continual ebullition of metal collecting in the mould which results from the high vacuum exerted close to the mould cavity.

If desired, degassing may be continued after pouring is complete since the pouring interval is relatively brief and about twenty minutes or so lapses before heat of maximum intensity has been conducted through the mould into the area of the seal. This may be accomplished by maintaining or renewing the vacuum after a suitable closure has been inserted in the basket and positioned over the upper side of the aperture in the transverse wall. After the degassing operation has been terminated and after the heat in the area of the seal is sufficient to decompose the sealing composition, the pouring box is disengaged so that the solidified ingot may be removed from the mould cavity.

The epoxy novolac resins useful in the present invention are produced by the epoxylation of a novolac type base resin which is a permanently fusible resin formed by the condensation of a phenol and an aldehyde, e.g. phenol and formaldehyde, in the presence of an acid catalyst. One of the methods conventionally used in the preparation of epoxy novolac resins comprises reacting the phenol-aldehyde condensate with an epihalohydrin, e.g. epichlorohydrin, in the presence of a basic catalyst. While any of the epoxy novolac resins may be used in the present composition, it is preferred to employ a liquid epoxy novolac resin in order to facilitate mixing with the other ingredients and to allow greater ease in application. A particularly suitable epoxy novolac resin has the approximate average general formula:



where  $n$  is about 0.2. This resin is further characterised as having an epoxide equivalent weight of 172—179, a molecular weight of 2.2 times the epoxide equivalent weight and a viscosity between about 1400 and 2000 centipoises at approximately 52°C.

The glycidyl polyethers used in admixture with the epoxy novolac resins to form the resin component are the liquid condensation pro-

ducts of polyhydric phenols, such as bis(4-hydroxyphenyl) dimethyl methane, and polyfunctional halohydrins, such as epichlorohydrin and glycerol dichlorohydrin, which have an epoxide equivalent weight between 350 and 450 and a Brookfield viscosity between 450 and 16,000 centipoises at 25°C. A preferred resin of this type is a diglycidyl ether of bis(4-hydroxyphenyl) dimethyl methane having one of its terminal epoxide groups reacted with glycerine and which has an epoxide equivalent weight between 375 and 410 and a Brookfield viscosity between 450 and 650 centipoises at 25°C. A typical glycerine-modified resin of this type is commercially available as "Epirez 507".

As is well known in the art, the epoxide equivalent weight represents the weight of resin in grams which contains 1 gram equivalent of epoxy. The value for the epoxide equivalent weight is conventionally determined by reacting a known quantity of resin with a known quantity of hydrochloric acid and back-titrating the remaining acid to determine its consumption.

The amount of glycidyl polyether resin used in admixture with the epoxy novolac resin is between 50 and 90%, preferably between 50 and 70%, by weight as based on the total weight of epoxy novolac and glycidyl polyether resins used. At least 50% by weight of glycidyl polyether resin is needed to impart the flexibility required in the cured composition to prevent the formation of minute cracks during handling and to allow easy dismantling of the casting equipment after pouring as well as easy removal of cured material from the mould groove. Above 90% by weight of glycidyl polyether resin, the cured composition does not have sufficient strength to hold an airtight seal in the presence of high vacuum at high temperatures.

In formulating the curing component for the epoxy resin mixture, any of the lower molecular weight resinous polyamides may be used which have an amine number greater than 85. The "amine number" is defined as the milligrams of potassium hydroxide equivalent to the amine alkalinity in one gram of sample. Polyamide resins having an amine number much below 85 are not sufficiently reactive with the epoxy resin component to impart the cured properties desired in the present system.

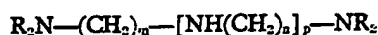
The resinous polyamides employed are prepared by methods well-known in the art by condensing polymeric polyene fatty acids, such as dimerized linoleic acid, and polyamines and, in general, have a viscosity between 40 and 575 poises at 40°C. as measured on a Brookfield Viscometer Model RVF at 20 RPM using a No. 3 spindle. Typical of the resins which may be used as the liquid polyamide resins, "Versamid 115", "Versamid 125" and "Versamid 140". Semi-fluid resins, such as "Versamid 100", may also be employed but are preferably used in admixture with the liquid resins in

minor proportions so that the resulting resin mix will have a workable room temperature viscosity. The preparation of the "Versamids" is described in U.S. Patent No. 2,379,413.

5 "Versamid" is a Registered Trade Mark.

In the present system the polyamides are used primarily for their plasticizing or flexibilizing effect on the cured composition. In order to obtain cured compositions having the strength and flexibility necessary for resisting mechanical shock, the resinous polyamide is used in amounts varying between 50 and 100 parts by weight on the basis of 100 parts by weight of epoxy novolac resin and liquid glycidyl polyether. When less than 50 parts is used, the cured composition tends to become gaseous, while compositions containing more than 100 parts of the polyamide resin become brittle, easily cracked materials.

20 Though the polyamide resin imparts cured properties to the composition, the use of an amine curing agent for the epoxy resin component is essential for obtaining a relatively rapid cure over a wide temperature range. The amines and mixtures of amines employed have the following formula:



where each of m and n, which may be the same or different, is 1 to 6, p is 0 to 6, R represents a hydrogen atom or a lower alkyl group containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl and butyl, said amine or mixtures thereof having at least two active hydrogens. Illustrative amines include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, hexamethylene tetramine and 3-diethylamino-1-propylamine. The amount of amine used

should be sufficient for completely curing the epoxy novolac and glycidyl polyether resins. Normally, the amount employed is in slight excess of the stoichiometric amount needed for cure since some of the amine is frequently lost through volatilization during curing. On the other hand, large excesses should preferably be avoided since excess amine tends to interfere with cross-linking.

From 30 to 50 parts by weight of magnesium silicate filler based on 100 parts by weight of the epoxy resin mixture have been found satisfactory. At least 30 parts are required to prevent the formation of minute cracks due to thermal expansion while amounts above 50 parts by weight tend to impair the cohesive properties and internal strength of the cured system.

The following Examples illustrate the invention, Examples 1, 2 and 7 being comparative Examples. All quantities given are in parts by weight unless specified otherwise.

#### EXAMPLES 1-7

For comparing flexibility and thermal decomposition characteristics, seven formulations were prepared wherein the resin components, except in Examples 1 and 7, contained varying amounts of glycidyl polyether resin in admixture with an epoxy novolac resin. The resin component of Example 1 contained the epoxy novolac resin as the sole epoxy resin while the resin component of Example 7 contained the glycidyl polyether resin as the sole epoxy resin. The separately prepared and packaged curing agents used for each of the seven resin components were identical.

The ingredients used in the resin components and their amounts are set forth in Table I below.

TABLE I

Ingredients	Examples (parts by weight)						
	1	2	3	4	5	6	7
Epoxyated phenol-formaldehyde resin (Epoxide equiv. wt. 172-179; Molecular wt. 2.2 times epox. equiv. wt.; Viscosity 1400-2000 cps. at 52°C.)	100	60	50	50	30	20	—
Glycerine-modified diglycidyl ether of bis(4-hydroxyphenyl) dimethyl methane-Epoxide equiv. wt. 375-410; Viscosity 450-650 cps. at 25°C.	—	40	50	50	70	80	100
Asbestine — finely divided magnesium silicate (filler)	25	25	35	45	30	30	30

Each resin component was prepared by mixing the two epoxy resins in a paddle mixer and adding the asbestine to the resin or resin mixture with stirring. After the addition of  
5 filler was complete, stirring was continued until

a uniform dispersion was obtained.

The curing component used for each of the above resin components was composed of the following:

	Ingredients	Parts by Weight
10	Liquid polyamide resin ("Versamid No. 115" — Amine No. 230—246 Viscosity — 575 poises at 40°C.)	92
	Liquid polyamide resin ("Versamid No. 125" — Amine No. 330—360 Viscosity 100 poises at 40°C.)	4
	Diethylene triamine	10.8

The curing components were prepared by mixing the polyamide resins and amine in a paddle mixer until a homogeneous mixture was obtained. Thereafter, the resin and curing components for each example were thoroughly blended.  
15

To compare the sealing performance of Examples 1 to 7 each composition was poured into the groove of a cast iron ingot mould heated to about 260°C. The pouring box was then seated on the mould so that the lower edge of the box was embedded in the sealing composition contained within the groove. Under these conditions each composition cured within a few minutes. Thereafter, the casting apparatus was allowed to stand at room temperature until it had cooled to about 120°C., at which time the mould and lower section of the box were evacuated and molten steel was introduced into the mould cavity.  
20 25 30

From repeated test runs, micron gauge readings below 100 microns could not be consistently obtained with the cured compositions of Examples 1, 2 and 7. The cured composition of Example 7, though possessing the requisite flexibility and curing characteristics, did not have sufficient heat resistance, i.e. resistance to melting, to hold a satisfactory seal at high vacuums and within the relatively high temperature range encountered during cooling of the apparatus and again during the pouring procedure.  
35 40

The compositions of Examples 1 and 2, like that of Example 7, possessed satisfactory curing characteristics under commercial conditions. However, minute cracks tended to form in the seal, which was attributed partly to mechanical and thermal stress and strain encountered during handling and cooling of the casting apparatus before pouring and partly to cured material remaining in the mould groove from prior seals. Though much of the cured material could be removed from the groove after each test, it was extremely difficult to remove all  
45 50

of the cured resin of Examples 1 and 2 after each test since the temperature in the area of the groove after pouring was not sufficient to decompose these compositions to any appreciable extent.  
55

In contrast, the seals formed from the compositions of Examples 3 to 6 consistently gave micron gauge readings of 100 microns and below in repeated tests in the presence of mechanical shock and over the broad temperature range encountered during cooling of the assembled apparatus and during pouring of the ingot. Also, it was found that the cured compositions of Examples 3 to 6 decomposed to the desired extent after each pouring run so that the mould groove could be easily and completely freed of cured material while still possessing the heat resistance required to maintain a substantially airtight seal during the pouring interval. In further tests, it was found that the compositions of Examples 3 to 6 cured in about one-half hour at 65°C. and about two hours at room temperature (20°C.) so that seals could be formed in a reasonably short time at low temperatures and high temperatures alike.  
60 65 70 75 80

From the above Examples and results obtained it is readily apparent that epoxide sealing compositions having a resin component containing 50% to 90% by weight of the selected glycidyl polyether resin in admixture with an epoxy novolac resin can be cured in relatively brief times over a wide temperature range to give strong, airtight metal-to-metal seals. In addition to excellent curing properties, these compositions in their cured state possess the requisite balance between flexibility and heat resistance required for commercial ingot casting operations. They are capable of withstanding cracking due to severe jarring of the pouring apparatus as frequently encountered in commercial pouring procedures and are sufficiently heat-resistant to provide a high vacuum seal during the pouring interval though  
85 90 95

decomposing to the extent necessary to allow easy removal of cured material from the groove after the ingot has been poured.

WHAT WE CLAIM IS:—

- 5 1. A cured epoxy resin composition derived from
  - (A) 100 parts by weight of a resin mixture of
    - 10 (1) 10 to 50% by weight of a liquid epoxy novolac resin and
    - 15 (2) 50 to 90% by weight of a liquid glycidyl polyether of a polyhydric phenol having an epoxide equivalent weight between 350 and 450;
  - (B) 30 to 50 parts by weight of finely divided magnesium silicate;
  - (C) between 50 and 100 parts by weight of a liquid resinous polyamide having an amine number of at least 85; and
  - 20 (D) at least one amine which is a curing agent for the resin mixture (A) in an amount in excess of that necessary to react stoichiometrically with said resin mixture and has the formula



- 25 wherein each of m and n, which may be the same or different, is 1 to 6, p is 0 to 6, R represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, said amine having at least
- 30 two active hydrogens.

- 2 2. A composition according to Claim 1 wherein the epoxy novolac resin has an epoxide equivalent weight between about 172 and 179 and a molecular weight of 2.2 times the
- 35 epoxide equivalent weight.

- 3 3. A composition according to Claim 1 or 2 wherein the amine is one or more of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, hexamethylene tetramine and 3-diethylamino-1-propylamine.
- 40 4. A composition according to any one of the preceding claims wherein liquid glycidyl polyether is a glycidyl polyether of bis(4-hydroxyphenyl)dimethyl methane having an
- 45 epoxide equivalent weight between 375 and 410.

- 5 5. A composition according to Claim 4 wherein the resin mixture (A) contains (1)
- 50 between 30 and 50% by weight of said epoxy

novolac resin and (2) between 50 and 70% by weight of said glycidyl polyether of bis(4-hydroxyphenyl)dimethyl methane having an

6. A cured epoxy resin composition derived from

- 55 (A) 100 parts by weight of a resin mixture of
  - (1) 30% by weight of a liquid epoxy novolac resin having an epoxide equivalent weight between 172 and 179 and a molecular weight of 2.2 times the
  - 60 epoxide equivalent weight and
  - (2) 70% by weight of a liquid glycidyl polyether of bis(4-hydroxyphenyl) dimethyl methane having an epoxide equivalent weight between 375 and 410;
  - 65 (B) 30 parts by weight of finely divided magnesium silicate,
  - (C) a mixture of polyamide resins consisting of
    - 70 (3) 92 parts by weight of a liquid resinous polyamide having an amine number between 230 and 246 and
    - (4) 4 parts by weight of a liquid resinous polyamide having an amine number between 330 and 360 and
    - 75 (D) 10.8 parts by weight of diethylene triamine.

7. A cured epoxy resin according to Claim 1 substantially as hereinbefore described.

8. A cured epoxy resin according to Claim 1 substantially as described in any one of
- 80 Examples 3, 4 or 6.

9. A vacuum casting apparatus wherein the seal between the ingot mould and the removable pouring box is formed by a composition as claimed in any one of the preceding claims.
- 85 10. Process for the production of a cured epoxy resin composition as claimed in any one of claims 1—8 which comprises mixing a first component comprising constituents (A) and
- 90 (B) and a second component comprising constituents (C) and (D).

11. A two-component pack for use in a process as claimed in Claim 10 in which the first component comprising constituents (A) and (B) is physically distinct from the second
- 95 component comprising constituents (C) and (D).

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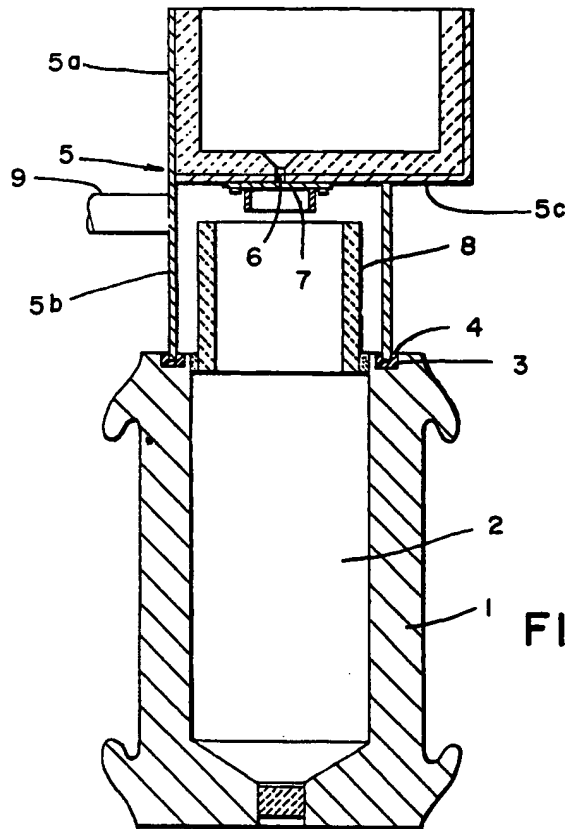


FIG. 1

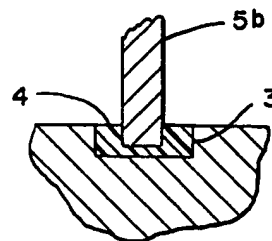


FIG. 2